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OXIDATION OF THIOSALTS WITH HYDROGEN PEROXIDE

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MICROMEDIA

OXIDATION OF THIOSALTS WITH HYDROGEN PEROXIDE

by

E. Rolia*

ABSTRACT

A method was developed to oxidize thiosalts to sulphate in neutral to weakly acidic media using hydrogen peroxide in the presence of a ferrous ion catalyst. Mechanisms and kinetics of oxidation are briefly discussed and considered in terms of the technical implementation of a process for the year-round treatment of mill effluents of the Brunswick Mining and Smelting Corporation. The reagent cost for treating a 10,000 L/min effluent stream containing 1000 mg/L S_2O_3 is fixed mainly by the high H_2O_2 requirements, and is estimated to be about $8.5 M/Y. The process is recommended as a clean up stage only, in combination with or as a sequel to a more cost efficient method for removal of the bulk of the thiosalts.

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OXYDATION DES THIOSELS AVEC DU PEROXYDE D'HYDROGÈNE

par

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Résumé

On a développé une méthode pour oxyder les thiosels en sulfates dans un milieu à indice d'acide allant de neutre à faible, en utilisant du peroxyde d'hydrogène en présence d'un catalyseur d'ions ferreux. Ce rapport contient un bref examen des mécanismes et vitesses d'oxydation en relation avec la mise en oeuvre technique d'un procédé de traitement permanent des effluents des usines de la Brunswick Mining and Smelting Corporation. Le coût du réactif pour le traitement d'un effluent ayant un débit de 10 000 L/min et contenant 1000 mg/L de S_2O_3 est déterminé principalement par la grande quantité de H_2O_2 exigée; on en a estimé ce coût à 8,5 millions de dollars par an. On recommande d'utiliser le procédé uniquement comme étape d'épuration en conjugaison avec ou pour faire suite à une méthode plus rentable pour enlever la majeure partie des thiosels.

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INTRODUCTION

A cost-effective method is sought to treat the mill effluent from the Brunswick Mining and Smelting Corporation, New Brunswick (BMS) that contains thiosalts in the range of 600-2000 mg/L, at an effluent flow rate of about 10,000 L/min. Thiosalts are partially oxidized sulphur compounds; e.g., thiosulphate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) that are generated in the milling of sulphide ores (1,2,3). Mill effluents are usually impounded in tailings ponds where the thiosalts are oxidized to sulphuric acid. Tha natural oxidation process is slow in summer and hardly occurs at all in the winter. If the effluent is discharged to rivers and lakes, gradual oxidation occurs and the generated sulphuric acid creates a pollution problem (4).

The removal of thiosalts by air or oxygen at elevated temperatures and pressures (5) or by metallic iron (6) has been considered. Polluting and acid-generating oxidants such as Cl_2, NO, SO_2/O_2 should be avoided, and other physico chemical methods (e.g., reverse osmosis, electrodialysis, electro-oxidation, ion exchange, carbon adsorption, etc.) were deemed less suitable (3,8). Bacterial oxidation appeared to be promising although there are technical problems (7) associated with its use. The high output of thiosalts in relatively dilute concentrations generally results in high reagent and operating costs. Process optimization is therefore required, and the oxidation with hydrogen peroxide (H_2O_2) is presently discussed in detail within this framework.

The objectives of this study were to determine the amount of H_2O_2 which would be required to destroy thiosalts in the BMS mill effluent and to determine the effect of variables such as pH, thiosalt concentration, composition and temperature on the rate of reaction.

BACKGROUND

The chemistry of thiosalts is quite complex and difficult to define (3,8). Schmidt (9) developed consistent reaction models based on the delocalized electron structure of sulphur-sulphur bonds in different environments. He postulated that highly unstable intermediates are formed based on the structure: $S_xO_3^{2-}$ (sulfane-mono sulfonates), homolog of the stable thiosulphate. Reaction paths were determined by the nucleophillic strength of entering and leaving groups, and the reaction chains were terminated by oxidation or elimination of the terminal sulphidic group. Thus, the dependence of the final products on the pH and Eh of the media, as well as on the temperature, presence of catalysts and nucleophillic reagents, can be qualitatively understood.

The oxidation of thiosalts by H_2O_2 can be classified as incomplete or complete (10). The first type of oxidation leads to "higher" thiosalts and OH^- formation; e.g.;

$$2S_2O_3^{2-} + H_2O_2 \longrightarrow S_4O_6^{2-} + 2OH^- \quad (1)$$

$$3S_2O_3^{2-} + 4H_2O_2 \longrightarrow 2S_3O_6^{2-} + 2OH^- + 3H_2O \quad (2)$$

The second type of oxidation generates sulphuric acid; e.g.,

$$S_2O_3^{2-} + 4H_2O_2 \longrightarrow 2SO_4^{2-} + 2H^+ + 3H_2O \quad (3)$$

$$S_3O_6^{2-} + 4H_2O_2 \longrightarrow 3SO_4^{2-} + 4H^+ + 2H_2O \quad (4)$$

$$S_4O_6^{2-} + 7H_2O_2 \longrightarrow 4SO_4^{2-} + 6H^+ + 4H_2O \quad (5)$$

It is, therefore, not surprising that the oxidation of thiosulphate in weakly acidic solutions tends to stop at the thionate stage, unless a catalyst such as Fe^{2+} is present (10,11).

The system H_2O_2/Fe^{2+} is known as Fenton's reagent, and its oxidizing strength can be explained by the Haber-Weiss reaction scheme (12):

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH^\cdot \quad (6)$$

$$OH^\cdot + H_2O_2 \longrightarrow HO_2^\cdot + H_2O \quad (7)$$

$$HO_2^\cdot + H_2O_2 \longrightarrow O_2 + H_2O + OH^\cdot \quad (8)$$

The perhydroxyl ($HO_2^\cdot$) and especially the hydroxyl ($OH^\cdot$) radicals are strong oxidizing agents due to their high electron affinities, and are the chain carriers in the autodecomposition of H_2O_2 as well. It was suggested that the weaker catalytic activities of other heavy metal ions are based on similar mechanisms; e.g.,

$$H_2O_2 \rightarrow H^+ + HO_2^- \quad (9)$$

$$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2^\cdot \quad (10)$$

The primary step is always a redox reaction resulting in radical formation. A local excess of reductants favours chain termination, whereas a local excess of H_2O_2 favours chain propagation.

Equations 3 to 5 indicate that the complete oxidation of thiosalts will result in high reagent and neutralization costs for the process. These requirements could be drastically reduced if elemental sulphur were produced; e.g., at elevated temperatures in neutral solutions (13), by U.V. induced oxidation (3), or in the presence of H_2S (8). However, additional energy or operating costs may arise, and the production of elemental sulphur is generally a minor side reaction. The removal of colloidal sulphur might be a problem.

The incomplete oxidation by Fenton's reagent, as patented by Ohtani et al. (11), also reduces the H_2O_2 and neutralization requirements. The product effluent is, however, still unacceptable since the thionates will continue to generate acid given a long enough reaction time.

EXPERIMENTAL

Tests were conducted on samples of BMS mill effluents and on synthetic solutions. Analytical grade reagents were obtained from commercial suppliers, and $K_2S_3O_6$ was synthesized in the laboratory (3). The 30% w/w H_2O_2 solution was analysed by a standard iodometric method (14) and contained 10 mmol H_2O_2 per mL of solution.

Thiosalt concentrations were determined as S_2O_3 by the acidimetric titration of acid formed by mercuric chloride oxidation (3):

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HgCl_2 \cdot 2HgS + 4H^+ + 4Cl^- + 2SO_4^{2-} \quad (11)$$

$$2S_xO_6^{2-} + 3HgCl_2 + 4H_2O \rightarrow HgCl_2 \cdot 2HgS + 8H^+ + 4Cl^- + 4SO_4^{-} + (2x-6)S \quad (12)$$

According to these equations, each mol of thionate would be determined as the equivalent of 2 mol $S_2O_3^{2-}$. For complete oxidation (see equations 3 to 5), the expected relationships per mol of thiosalt are given in Table 1.

Table 1 - Calculated H_2O_2 requirements for the complete oxidation of various thiosalt species

Thiosalt Species	Titration (mol)		Oxidation (mol)		Oxidation (mol ratios)	
	H^+	S_2O_3	H^+	H_2O_2	H^+/S_2O_3	H_2O_2/S_2O_3
$S_2O_3^{2-}$	2	1	2	4	2	4
$S_3O_6^{2-}$	4	2	4	4	2	2
$S_4O_6^{2-}$	4	2	6	7	3	3.5

S_2O_3 (without the ionic charge) is used throughout this report to indicate the titrated thiosalt equivalent or its difference before and after each test.

Reactions were conducted in a 2 L open beaker, equipped with baffles and a magnetic stirrer mechanism. The course of the reactions was followed by monitoring the pH of the test solutions. The utilization of H_2O_2 was determined as the H_2O_2/S_2O_3 molar ratio as defined above. Since substoichiometric amounts of H_2O_2 were added, completion of the reactions was indicated by a levelling off in pH values.

RESULTS AND OBSERVATIONS

Test results are summarized in Tables 2 and 3, and further details are listed below in chronological order.

TEST 1

BMS effluent from barrel 1 had a pH reading of 5.50 and a thiosalt assay of 209 mg/L as S_2O_3. To a 1800 mL sample was added 10 mmol H_2O_2. The rate of drop in pH is shown in Figure 1. The curve shows a rapid drop in pH, and a constant pH was reached in ∿12 min. As soon as H_2O_2 was added, the solution turned yellow, and the colour disappeared as the pH approached 3.0. Residual thiosalts assayed 38 mg/L S_2O_3, yielding a H_2SO_3 molar ratio of 3.6/1.

TEST 2

Another 1800 mL sample of the same effluent was spiked with 1 mmol potassium tetrathionate. The pH dropped rapidly as in Test 1, but the yellow colour disappeared more quickly. There was an odour of H_2S and some elemental sulphur precipitated. The H_2O_2/S_2O_3 molar ratio was 3.2.

Table 2. Tests with BMS effluents at room temperature
1-5:barrel 1, containing 1.87 mmol/L S_2O_3 at pH 5.5
6,9:barrel 2, containing 4.21 mmol/L S_2O_3 at pH 6.05
13,14:barrel 3, containing 6.53 mmol/L S_2O_3 at pH 6.9

Test	Thiosalts added		Reagents (mmol/L)		Time min	Final pH	H_2O_2/S_2O_3 mol ratio
	Species	mmol/L	H_2O_2	Fe^{2+}			
1	-	-	5.5	-	12	2.9	3.6
2	S_4O_6	0.56	11.1	-	∿10		3.2
3	S_3O_6	0.56	10.0	-	∿10		2.8
4	S_2O_3	2.0	11.1	-	180	2.5	3.6
5	S_2O_3	2.0					
	$+S_3O_6$	0.5					
	$+S_4O_6$	0.5	13.3	-	120	2.45	3.1
6	-	-	10.0	-	1080	5.4	7.8
9	-	-	8.9	0.29	6	2.7	3.5
13a	-	-	22.5	0.30	100	6.5	
b	-	-	22.5	0.61	100	6.0	
c	-	-	22.5	1.11	80	2.5	
d	-	-	22.5	1.20	10	2.5	3.75
e	-	-	22.5	1.40	2	2.4	
14a	-	-	22.5	1.40	<1	2.5	3.60 (60°C)
b	-	-	22.5	1.40	10	2.5	3.70 (6°C)

Table 3. Tests conducted on synthetic solutions

Test	Thiosalt Added		Reagents (mmol/L)		Oxidation (mol ratios)	
	Species	mmol/L	H_2O_2	$FeSO_4$	H_2O_2/S_2O_3	H^+/S_2O_3
7	S_3O_6	1		after		
	$+S_4O_6$	1	11.1	2 h	n.a.	n.a.
8a	S_2O_3	4	7.5	0.07	4.2	n.a.
b	S_3O_6	2	8.6	0.04	1.8	n.a.
c	S_4O_6	2	8.3	0.05	2.5	n.a.
10a	S_2O_3	8.3	26.1	0.41	3.8	n.a.
b	S_3O_6	5	15.3	0.56	2.0	n.a.
c	S_4O_6	5	11.1	0.56	3.0	n.a.
11a	S_2O_3	10	33.3	0.61	n.a.	1.8
b	S_3O_6	5	18.3	0.56	n.a.	2.4
c	S_4O_6	4.4	26.7	0.56	n.a.	2.7
12	S_2O_3	5				
	$+S_3O_6$	2.5	26.1	0.59	2.8	2.3

TEST 3

A third 1800 mL sample of effluent was spiked with 1 mmol potassium trithionate. The pH dropped rapidly as in Tests 1 and 2, and there was only a fleeting glimpse of yellow colour. After a prolonged period, a light precipitate of elemental sulphur was formed as a suspension in solution. The H_2O_2/S_2O_3 molar ratio was 2.8.

TEST 4

An 1800 mL sample of effluent was spiked with 2 mmol $Na_2S_2O_3$. The solution assayed 433 mg/L S_2O_3. When H_2O_2 was added, the reaction was very slow as shown in Figure 2. The solution turned yellow and there was initially a rise in pH. The solution became colourless at 2.8 h when the pH was 2.7. Elemental sulphur precipitated. Residual thiosalts in the final solution assayed 81 mg/L S_2O_3. The H_2O_2/S_2O_3 molar ratio was 3.5.

TEST 5

This test was performed to confirm the slower oxidation of thiosulphate compared to trithionate and tetrathionate. An 1800 mL sample of effluent was spiked with 2 mmol/L $Na_2S_2O_3$, 0.5 mmol/L $K_2S_3O_6$ and 0.5 mmol/L $K_2S_4O_6$. Total thiosalt concentration was 644 mg/L S_2O_3. To the solution was added 24 mmol H_2O_2. The change in pH is shown in Figure 3. The solution was yellow for 1.6 h when the colour disappeared. There was an odour of H_2S and elemental sulphur precipitated. The pH of the final solution was 2.45 and residual thiosalts were 166 mg/L S_2O_3. Comparison of the curves in Figure 3 and in Figure 2 shows faster oxidation kinetics in the presence of polythionates.

TEST 6

BMS effluent from the second barrel was at pH 6.05 and the thiosalt concentration was 472 gm/L S_2O_3. To 1800 mL of sample was added 18 mmol H_2O_2. The change in pH is shown in Figure 4. There was initially a rise in pH and in 3 h the pH was 6.50. The test solution was allowed to stand overnight. In the morning a yellow oil settled to the bottom of the beaker. The pH of the decanted solution was 5.4 and the residual thiosalts were 328 mg/L S_2O_3. The molar ratio H_2O_2/S_2O_3 was 7.8, and this might indicate that unreacted H_2O_2 was present in the yellow oil or that autodecomposition of H_2O_2 had occurred upon standing.

TEST 7

It is known that trace quantities of Zn, Mn, Fe, Cu or Pb may be present in BMS effluent. Manganous sulphate and ferrous sulphate were added separately to observe their effects on the oxidation of polythionates. To 1800 mL of distilled water were added 1.8 mmol $K_2S_3O_6$, 1.8 mmol $K_2S_4O_6$ (polythionates oxidized rapidly in Tests 2 and 3) and 20 mmol H_2O_2. The results for $FeSO_4$ are shown in Figure 5 (manganous sulphate had no effect on the reaction). When $FeSO_4$ was added at 2.0 h the drop in pH was rapid.

TEST 8

This test was performed to observe the effect of ferrous sulphate on the oxidation of individual thiosalt species in distilled water with H_2O_2. The results are shown in Figure 6. Tetrathionate (2 mmol/L) and trithionate (2 mmol/L) were both oxidized in the presence of 3 mg Fe^{2+}/L. Thiosulphate (4 mmol/L) oxidized at a slower rate when the concentration of Fe^{2+} was below 10 mg/L. The results show that the three thiosalt species can be oxidized rapidly in the presence of ferrous sulphate. For $Na_2S_2O_3$, $K_2S_3O_6$ and $K_2S_4O_6$ the molar ratios H_2O_2/S_2O_3 were 4.2, 1.8 and 2.5, respectively.

TEST 9

This test was done to observe the effect of $FeSO_4$ on the oxidation of thiosalts in effluent from barrel 2. Previously (Test 6, Figure 4) the effluent had to stand many hours for the thiosalts to react with H_2O_2. To 1800 mL of effluent were added 16 mmol H_2O_2 and 16 mg Fe^{2+}/L as ferrous sulphate. The rate of drop of pH is shown in Figure 7. The results indicate that in the presence of ferrous sulphate, thiosalts are rapidly oxidized by H_2O_2. The molar ratio H_2O_2/S_2O_3 oxidized was 3.5.

TEST 10

This test was conducted to determine the H_2O_2/S_2O_3 ratio required for complete oxidation of high concentrations of individual thiosalts ($\sim$1000 mg/L S_2O_3) in distilled water. Ferrous sulphate (31 mg Fe^{2+}/L) was also added. A summary of experimental conditions and molar ratios found in Tests 8 and 10 is given in Table 3. The results show that the molar ratio H_2O_2/S_2O_3 at the higher thiosalt concentrations is about the same as at the lower thiosalt concentrations (Test 8). Less H_2O_2 is needed to oxidize polythionates than to oxidize an equivalent S_2O_3 amount of thiosulphate.

TEST 11

In the presence of sufficient ferrous sulphate, the major product of reaction of H_2O_2 with thiosalts is sulphuric acid. A test was performed to determine the quantity of acid produced in the reaction of individual thiosalts with H_2O_2. Ferrous sulphate was added as $\sim$3 mg Fe^{2+}/L for each 100 mg/L S_2O_3 present. The final solution was titrated with 1 N NaOH to pH 7-8. The effect of iron on the amount of base added was thought to be small. The results obtained are summarized in Table 4.

Table 4 - H_2SO_4 generated during the H_2O_2 oxidation of various thiosalt species

Thiosalt (1 mmol)	Generated H^+ ion mmol	H^+/S_2O_3 mol ratio
$Na_2S_2O_3$	2.0	1.8
$K_2S_3O_6$	4.2	2.4
$K_2S_4O_6$	6.1	2.7

Comparison with Equations 3-5 indicates that the amount of acid produced is nearly that predicted for the complete oxidation of the thiosalts.

TEST 12

A test was performed to determine the H_2O_2/S_2O_3 molar ratio and the quantity of acid formed by the oxidation of a mixture of thiosulphate and trithionate (molar ratio 2:1) that is approximately the thiosalt composition of BMS mill effluent (2). Total thiosalt concentration was 1053 mg/L S_2O_3. Ferrous sulphate was added to give 33 mg Fe^{2+}/L, and the results were:

- H_2O_2/S_2O_3 molar ratio was 2.8;
- H^+/S_2O_3 molar ratio was 2.3.

A duplicate test was performed except that 100 g/L of -100 mesh BMS bulk flotation concentrate was also added. The H_2O_2/S_2O_3 molar ratio was 2.9. The results indicate that the presence of sulphides does not increase the H_2O_2 consumption. A summary of experimental conditions and molar ratios H^+/S_2O_3 found in Tests 11 and 12 is given in Table 3.

TEST 13

The third barrel of effluent had a pH of 6.9 and a thiosalt concentration of 731 mg/L S_2O_3. In this test the effluent was used to determine the quantities of ferrous sulphate and hydrogen peroxide that are required to destroy the thiosalts as well as the amounts of acid generated.

To 1 L of effluent were added 18 mmol of H_2O_2 and different quantities of $FeSO_4$. The rate of drop of pH was monitored at 23°C, and the results are shown in Figure 8. The rate increased as the $FeSO_4$ concentration increased. At both 17 and 34 mg Fe^{2+}/L the reaction was very slow. At 62 mg Fe^{2+}/L there was initially a rapid drop in pH and then the reaction slowed. Oxidation was, however, complete in 10 min at 67 mg Fe^{2+}/L and in 3 min at 78 mg Fe^{2+}/L. In the presence of 62 mg Fe^{2+}/L, the curve suggests a reaction dependent on the formation of a catalytic agent since after a prolonged induction period (~60 min), there was a rapid drop in pH. In the presence of 78 mg Fe^{2+}/L, 22.5 mmol $H2O_2$ was added, and the final pH was 2.4. For the latter three iron concentrations the molar ratio H_2O_2/S_2O_3 was 3.75 and the molar ratio H^+/S_2O_3 was 2.15.

TEST 14

The rate of thiosalt oxidation was studied at a low temperature, 6°C, and at a high temperature, 60°C. In each test, 78 mg Fe^{2+}/L and 22.5 mmol H_2O_2 was added to 1000 mL of tailings effluent from barrel 3. The rate of drop of pH at 6°C is shown in Figure 9. The final pH of 2.5 was approached asymptotically; the reaction was complete in 10 min. The molar ratio H_2O_2/thiosalts oxidized was 3.70.

At 60°C, the pH dropped to 2.5 in less than 1 min. The molar ratio H_2O_2/thiosalts oxidized was 3.60.

DISCUSSION

The test results indicate that the course of oxidation can be conveniently followed by monitoring the pH. Incomplete oxidation of thiosulphate to thionate according to reactions 1 and 2 gives rise to a slight pH increase. Complete oxidation to sulphate according to reactions 3-5 results in a drastic pH drop, and the complete consumption of the added H_2O_2 is indicated by a levelling off of the pH curve.

The H_2O_2 utilization, expressed as the mol ratio of H_2O_2 added to the difference of titrated S_2O_3, is a function of the sulphur species present before and after the reaction, the degree of autodecomposition or other H_2O_2 losses (e.g., phase separation) during the course of the test. In general, the H_2O_2 consumption and acid generation values obtained correspond closely with the values expected from consideration of oxidation Equations 3-5 and titration Equations 11 and 12 (see Experimental section).

Test results on BMS effluent samples are summarized in Table 2. Tests 1-5 on effluents from barrel 1 (1.87 mmol/L S_2O_3, pH 5.5) indicate that the relatively fast oxidation kinetics are slowed significantly by the addition of thiosulphate (compare Tests 4 and 5, Figures 2 and 3, to Tests 1 to 3, Figure 1). Effluents from barrel 2 (4.21 mmol S_2O_3, pH 6.05) reacted much slower, Test 6, but the addition of 0.29 mmol Fe^{2+} in Test 9 accelerated the reaction significantly. It can, therefore, be argued that the effluent from barrel 1, containing relatively little S_2O_3 at a relatively low pH, contained some iron in solution that catalyzed the oxidation. The addition of thionates ($S_3O_6^{2-}$ or $S_4O_6^{2-}$) did not adversely affect the oxidation rate. The addition of thiosulphate was detrimental, probably because the partial oxidation to thionates increased the pH to 6.5, at which level iron might have been precipitated as hydroxide.

Tests 13a to c and 14a and b on effluents from barrel 3 (6.53 mmol/L S_2O_3, pH 6.9) seem to confirm this hypothesis. Thus, much more Fe^{2+} was required to catalyse the reaction at the higher pH, presumably to remove excess OH^- ions. Test 14b also showed that when enough Fe^{2+} is present in solution, the oxidation reaction still is complete within 10 min even at a temperature as low as 6°C.

Test results on synthetic solutions, summarized in Table 3, confirm the catalytic effect of Fe^{2+} ions. Since test solutions are better defined in this series, these results were used to confirm the stoichiometry of reactions 3 to 5, as well as the titration Equations 11 and 12. They also show that the catalytic oxidation of thiosalts in neutral to weakly acidic environments with H_2O_2/Fe^{2+} is very reliable as well as being quite insensitive to variations in initial concentrations of the individual thiosalt species.

The results from this study can be used to estimate approximately the reagent costs for destroying thiosalts in BMS effluents according to this process. Major items are H_2O_2 (61.4¢/lb, March 1984) and lime (CaO) for neutralization ($42.50/ton, March 1984), whereas the soluble iron requirements are based on purchased $FeSO_4.H_2O$ ($160.00/ton, March 1984). The basis of calculation is an effluent flow rate of 10,000 L/min containing 1000 mg/L S_2O_3 and having the mol ratios observed in Test 13 (H_2O_2/S_2O_3 = 3.75; H^+/S_2O_3 = 2.15; Fe^{2+}/S_2O_3 = 0.214).

S_2O_3 output = 10 kg/min = 5,781.6 T/y = 46.93 Mmol/y

H_2O_2 required = 176 Mmol/y = 6,581.7 T/y = $ 8.08 M/y

$Ca(OH)_2$ required = 50.45 Mmol/y = 3,118.7 T/y = $ 0.13 M/y

$FeSO_4.H_2O$ required = 10.06 Mmol/y = 1,880 T/y = $ 0.30 M/y

Total reagent costs: $ 8.51 M/y

The bulk of the reagent costs is for H_2O_2. Since H_2O_2 requirements can be reduced further only by producing more elemental sulphur (difficult to achieve) or by partial oxidation to the thionate stage (unacceptable), it is difficult to see how the hydrogen peroxide costs can be reduced significantly. Requirements for iron can be reduced by using an internal iron-containing stream and/or reducing the initial pH to about 5. The presence of iron would also be beneficial for removing the minor amounts of H_2S and S^o produced during the reaction.

CONCLUSIONS

The oxidation of thiosalts in BMS effluent by H_2O_2 and Fe^{2+} in weakly acidic media is technically feasible as a year-round operation. The H_2O_2 requirements in general are too high, however, for the method to be economically feasible if the total amount of thiosalts are to be treated by this route.

It is recommended that other suitable methods be used to remove the bulk of the thiosalts in a more economical manner, before H_2O_2-Fe^{2+} is used to eliminate the remnants of these environmentally undesirable compounds. Potentially suitable methods would include bacterial oxidation, aeration at high pH in the presence of catalysts or the use of multivalent oxidants such as ozone. Further brief testwork to explore these possibilities is planned.

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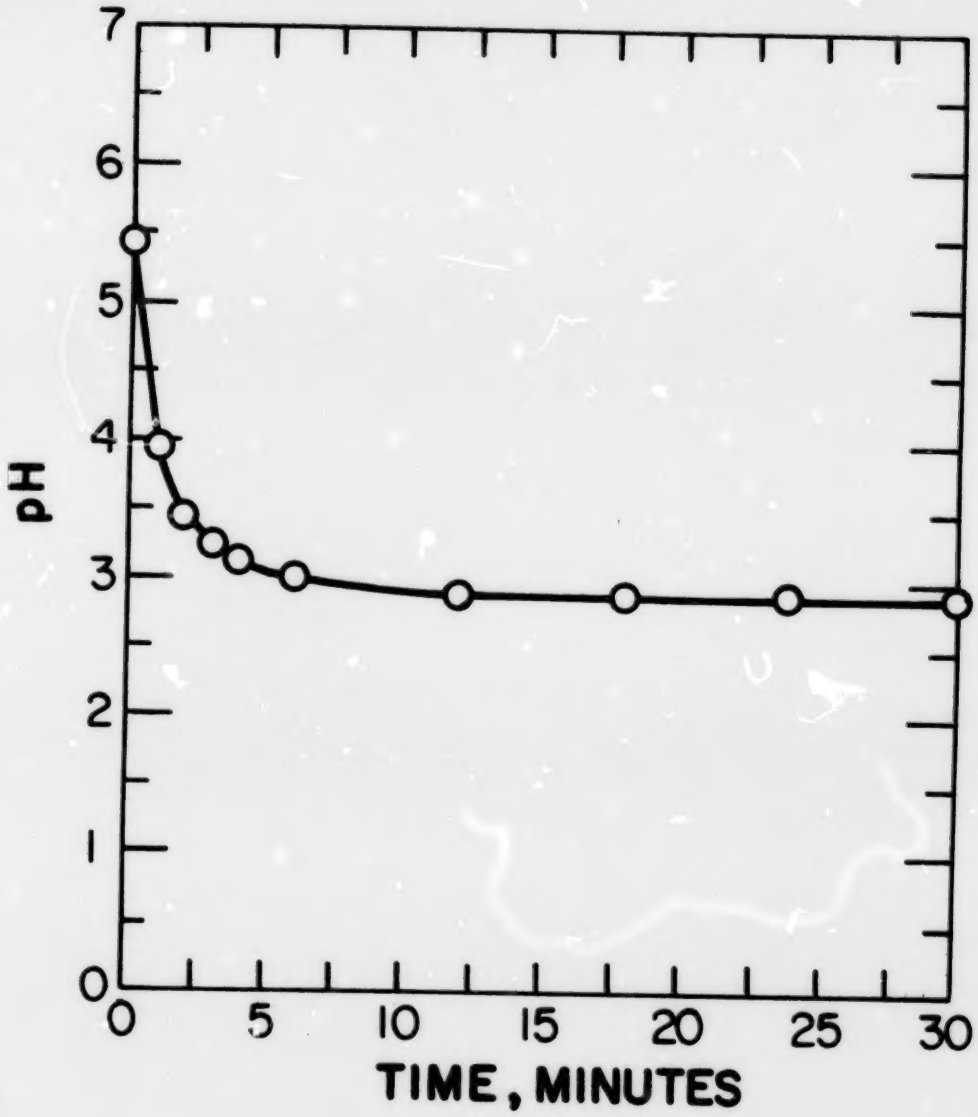

Figure 1. The H_2O_2 oxidation of BMS effluent from barrel 1 (1.87 mmol/L S_2O_3)

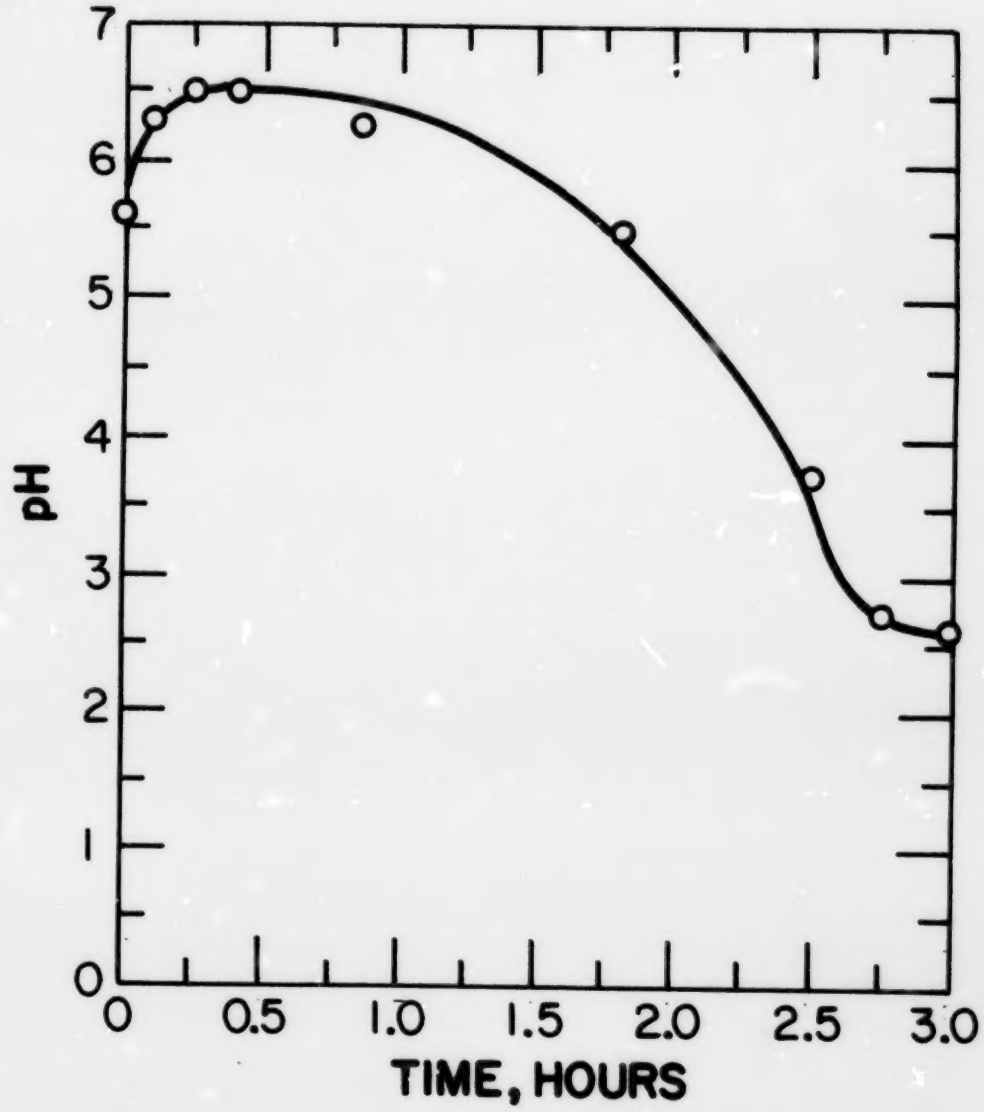

Figure 2. The H_2O_2 oxidation of BMS effluent from barrel 1, spiked with 2 mmol/L $Na_2S_2O_3$

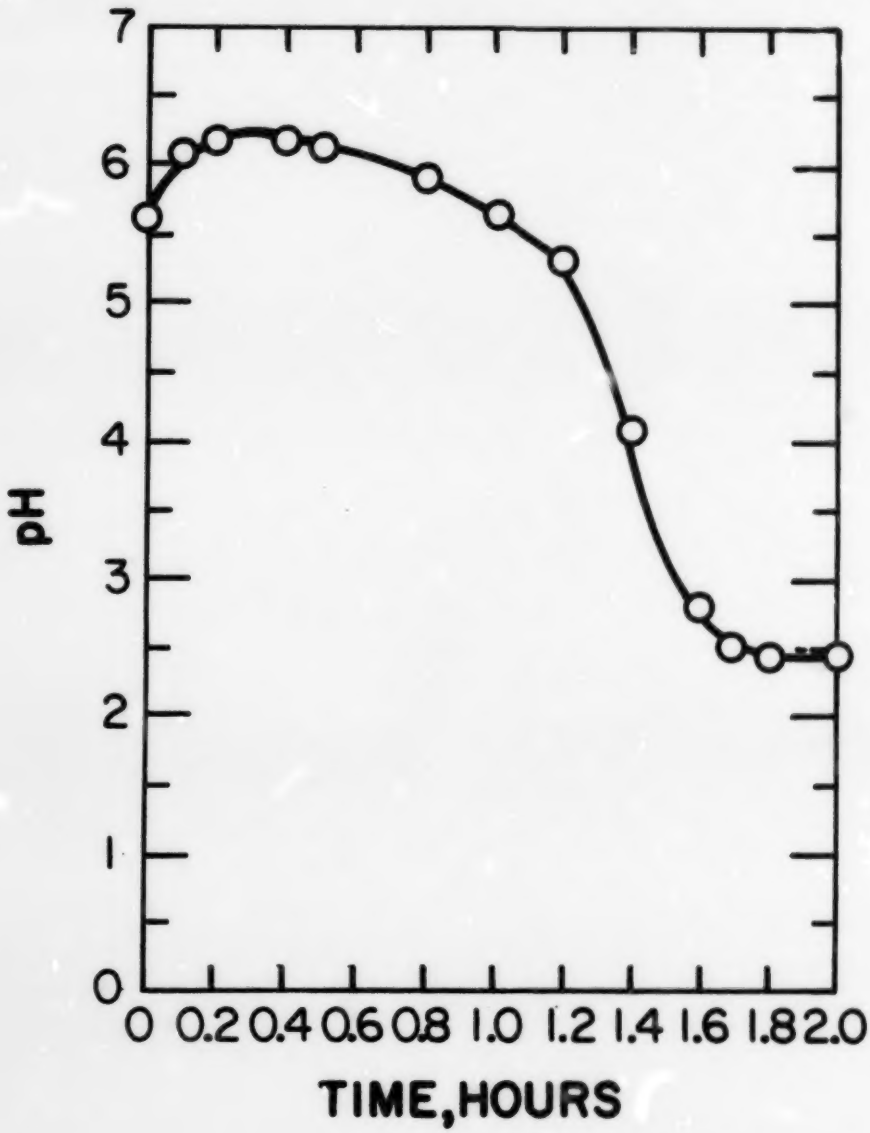

Figure 3. The H_2O_2 oxidation of BMS effluent from barrel 1, spiked with 1.1 mmol/L $Na_2S_2O_3$, 0.28 mmol/L $K_2S_3O_6$ and 0.28 mmol/L $K_2S_4O_6$

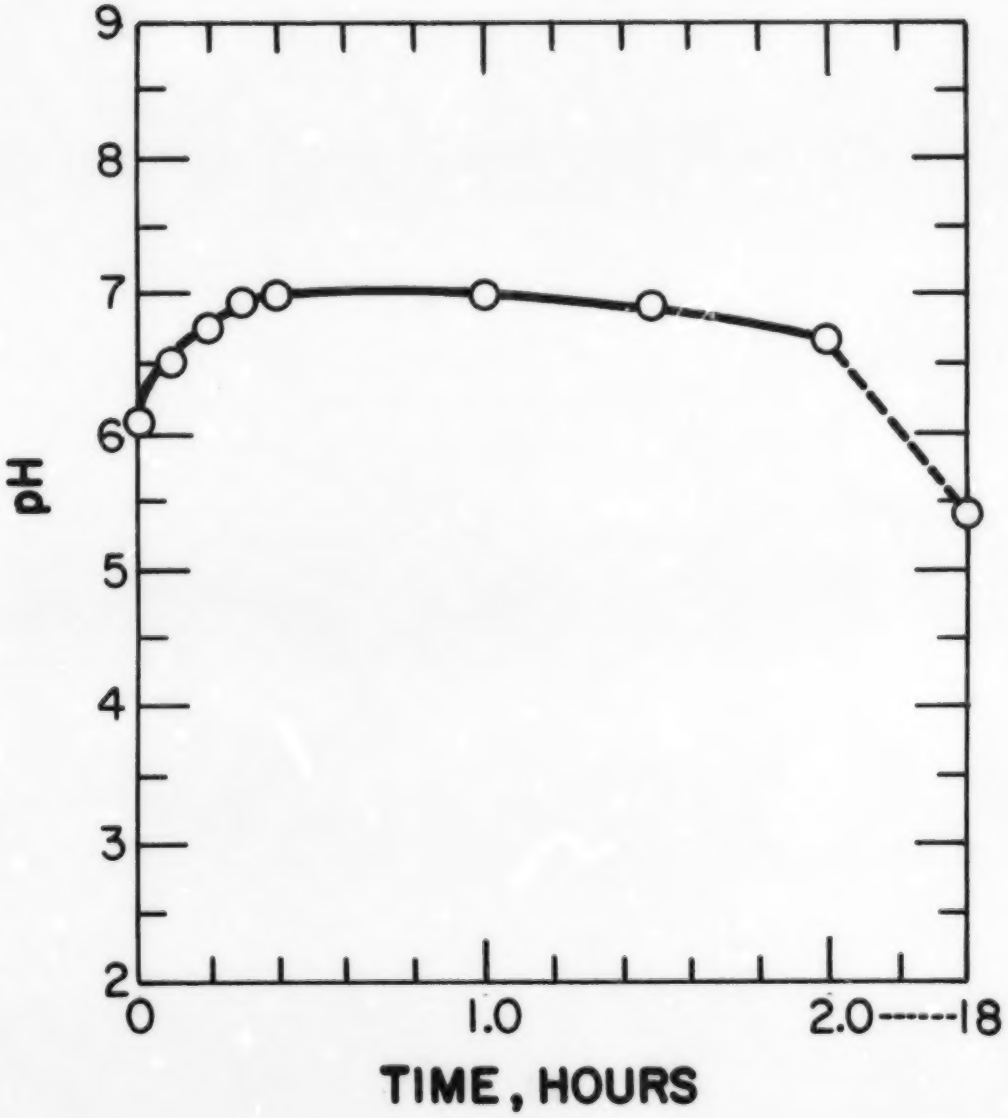

Figure 4. The H_2O_2 oxidation of BMS effluent from barrel 2

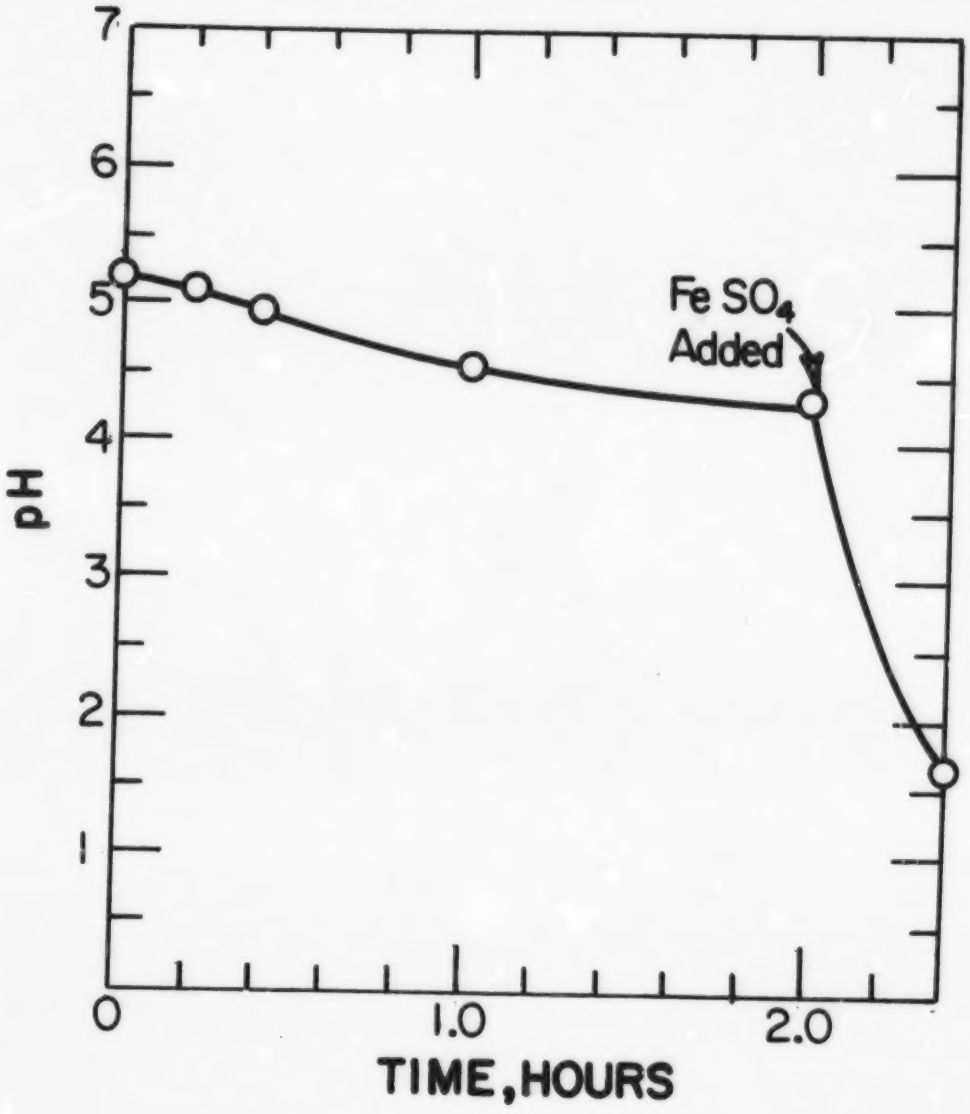

Figure 5. The H_2O_2 oxidation of a synthetic solution (1 mmol/L $K_2S_3O_6$ + 1 mmol/L $K_2S_4O_6$) and the effect of $FeSO_4$ addition after 2 h

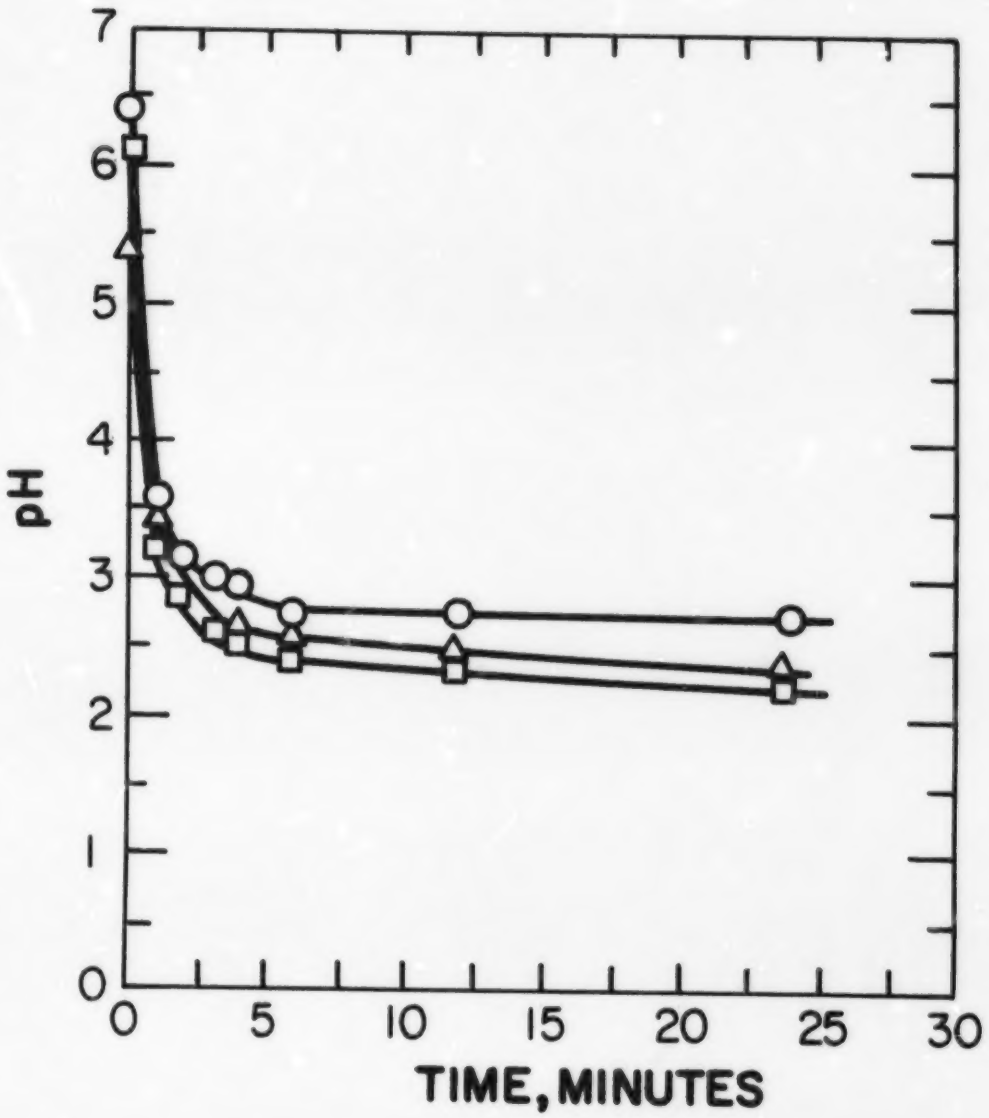

Figure 6. The H_2O_2 oxidation of individual thiosalts in the presence of $FeSO_4$ as catalyst; ● $S_2O_3^{2-}$ 430 mg/L; ▲ $S_3O_6^{2-}$ 407 mg/L; ▢ $S_4O_6^{2-}$ 437 mg/L

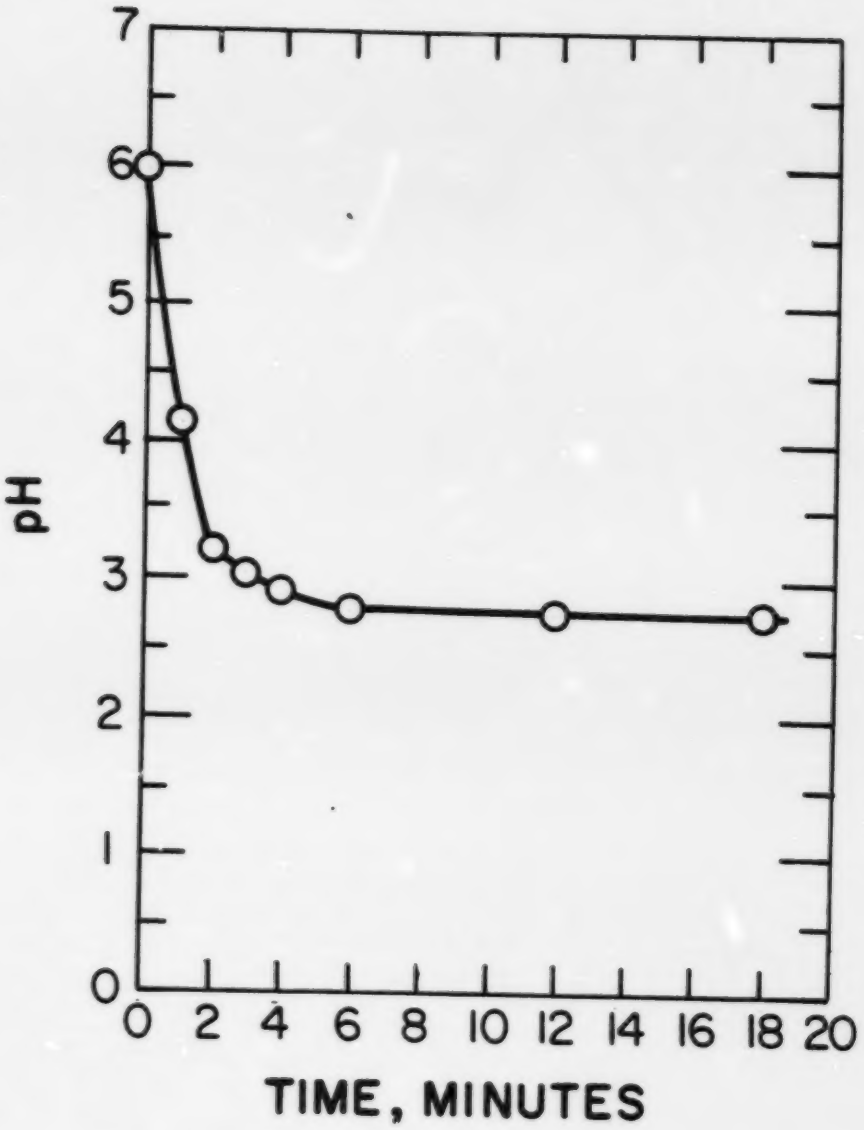

Figure 7. The oxidation of BMS effluent from barrel 2 in the presence of 0.29 mmol/L $FeSO_4$ as catalyst (same effluent as in Figure 4)

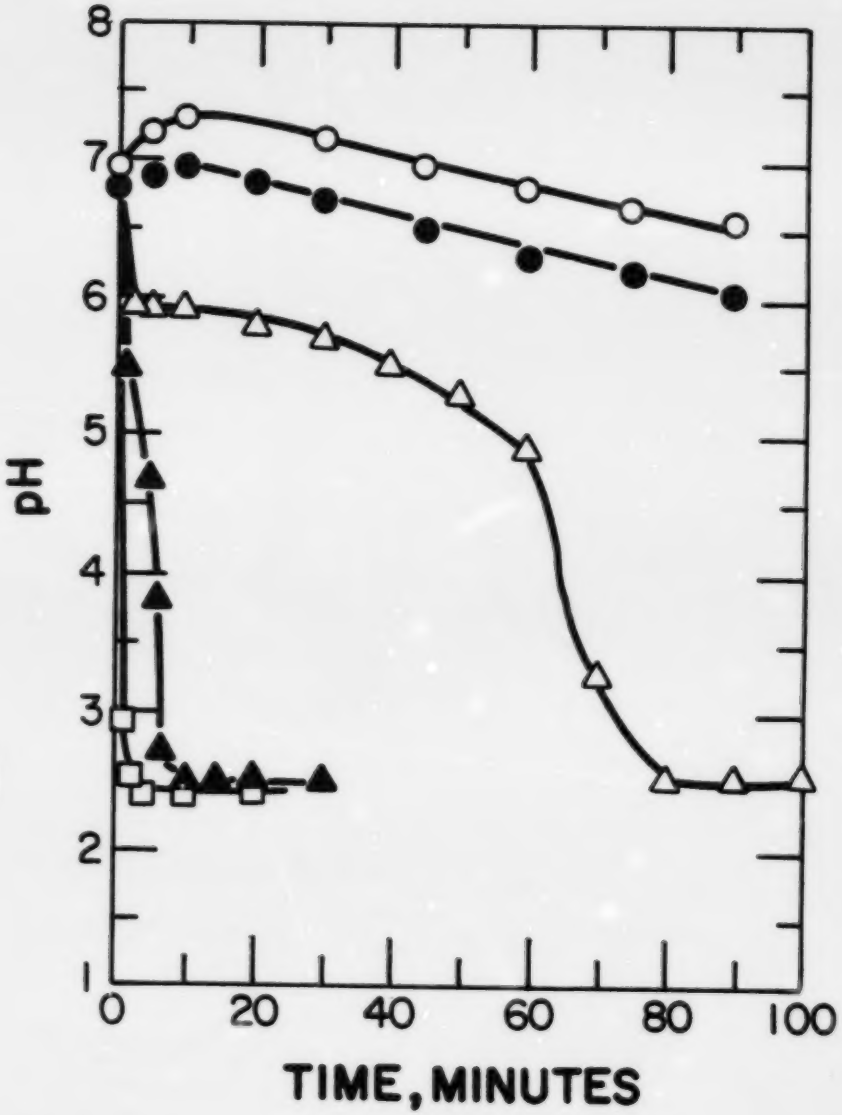

Figure 8. The oxidation of BMS effluent from barrel 3 (6.53 mmol/L S_2O_3) as a function of $FeSO_4$ additions. ○ 17 mg/L Fe^{2+}; ● 34 gm/L Fe^{2+}; ▲ 62 mg/L Fe^{2+}; ◭ 67 mg/L Fe^{2+}; ▱ 78 mg/L Fe^{2+}

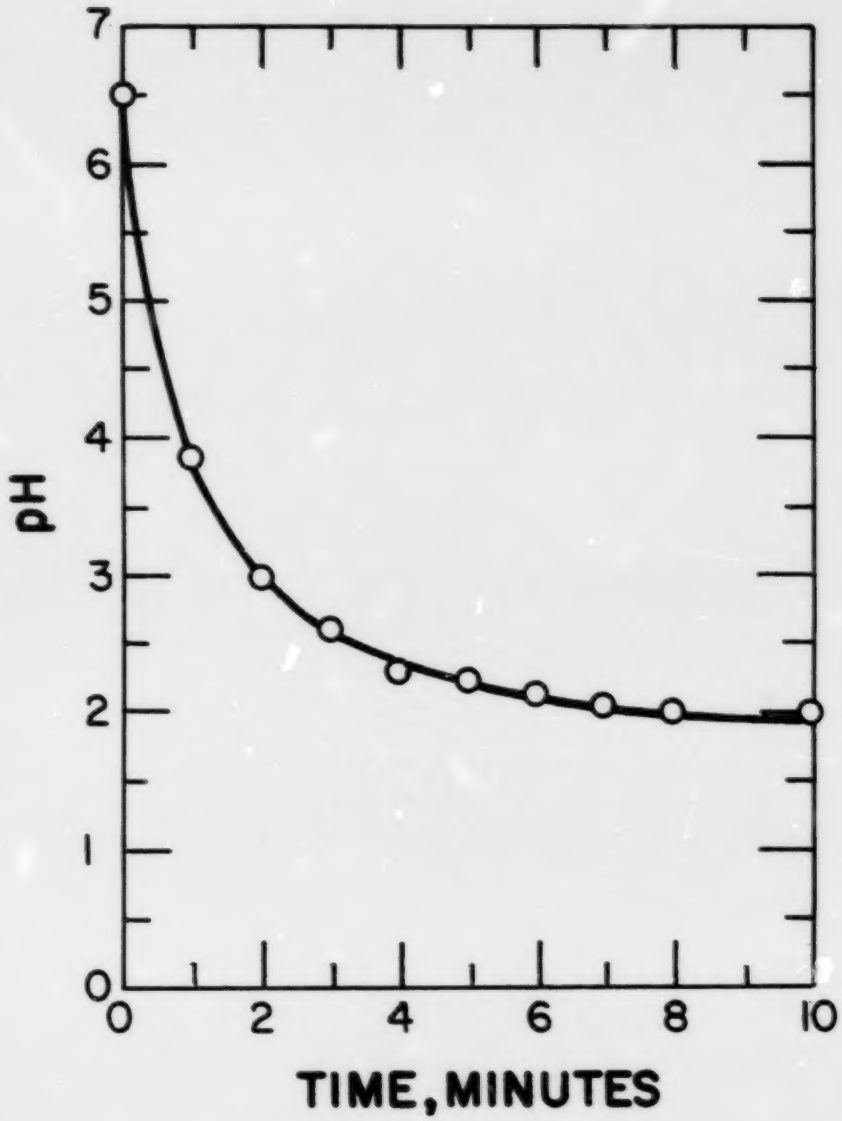

Figure 9. The H_2O_2 oxidation of BMS effluent from barrel 3, at 6°C in the presence of 1.4 mmol/L $FeSO_4$ as catalyst.